

# X-ray crystal structures of discrete and polymeric chiral silver complexes of monoterpenoid alkenes

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## Abstract

X-ray crystal structures are reported for five silver(I) complexes of four monoterpenoid alkenes. Discrete mononuclear complexes of the chiral alkenes (1S)-(–)- $\alpha$ -pinene and (1S)-(–)- $\beta$ -pinene with silver perchlorate and silver hexafluorophosphate are described. The achiral diene  $\gamma$ -terpinene forms a discrete mononuclear adduct with silver hexafluorophosphate and a two-dimensional polymeric network structure with silver triflate. The chiral diene (R)-(+)-limonene forms a one-dimensional chiral coordination polymer with silver hexafluorophosphate. In all structures the silver atom is  $\eta^2$ -bonded to the carbon–carbon bond(s) of the monoterpene with slightly longer bond distances to the more substituted carbon of the alkene moiety.

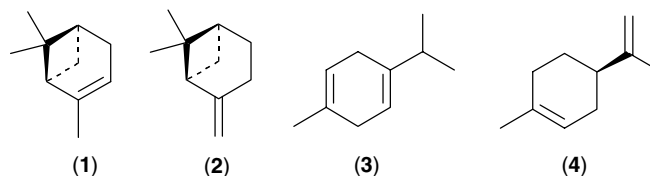
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**Keywords:** Silver; Alkene; Crystal structure; Bridging ligands; Self-assembly

## 1. Introduction

The use of combinations of organic ligands and metal ion precursors for the controlled self-assembly of metallo-supramolecular species have been the subject of much work in recent years [1]. Most commonly, this involves the use of bridging nitrogen-containing heterocyclic ligands with transition metal reactants to form various zero-, one-, two- or three-dimensional assemblies with diverse molecular architectures [2]. Of the many metals used, silver(I) salts have proved particularly popular in recent years [3]. Bridging ligands containing other donor atoms, such as oxygen and phosphorus, have also been used for this purpose. Recently, we have identified the silver–alkene interaction as a new metallosupramolecular synthon [4]. Alkenes have long been known to complex silver ions [5], a phenomenon commonly exploited in the chromatographic separation of alkenes [6]. However, the use of dienes (or polyenes) as bridging moieties for supramolecular assembly has not been previously investigated.

Coordination polymers are currently considered to offer considerable potential as functional constructs in the topical area of material science [7]. One such application is in the field of non-linear optics [8], wherein an important requirement for second-order non-linear optical properties is that the material be non-centrosymmetric. We believe that the simplest way to access non-centrosymmetric coordination polymers is to use chiral bridging ligands as synthons [9]. Within this context, we now report an extension of our recent use of achiral dienes as building blocks in silver metallosupramolecular chemistry [4] to the use of naturally occurring chiral alkenes and dienes as reactants for the construction of discrete and polymeric chiral assemblies. For this purpose we have chosen the readily available monoterpenoid alkenes (1) and (2) and dienes (3) and (4) as the organic reactants.



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## 2. Results and discussion

As a first step in this project we examined the reactions of the simple monoterpene alkenes (1S)-(-)- $\alpha$ -pinene (**1**) and (1S)-(-)- $\beta$ -pinene (**2**) with a variety of silver(I) salts. From such exploratory experiments two crystalline adducts **5** and **6** were obtained by reactions of silver perchlorate with excess **1** and silver hexafluorophosphate with excess **2**, in the presence of dichloromethane as a cosolvent. The complex **5** crystallizes in the orthorhombic space group  $P2_12_12_1$  and consists of two molecules of **1** bound to a silver atom that is also coordinated to an oxygen atom of the perchlorate counterion (Fig. 1). The silver atom has trigonal geometry with silver–carbon bond distances in the range 2.402(4)–2.515(4) Å. The distances to the more highly substituted carbons (C2 and C12) are longer than those to the less substituted (C3 and C13) carbons of the double bonds. Not unexpectedly, in both molecules of the monoterpene the silver atom coordinates to the face of the double bond that is *anti* to the bulky gem-dimethyl bridge. Thus, (1S)-(-)- $\alpha$ -pinene (**1**) readily forms a discrete 2:1 L:M complex in which the silver atom coordinates to the endocyclic double bond of the monoterpene.

The complex **6** crystallizes in the same space group and also has a  $L_2M$  stoichiometry. In this case the silver atom has a more linear geometry due to the much weaker interaction with the more weakly coordinating hexafluorophosphate counterion (Fig. 2). The silver–carbon distances are in the range 2.296(3)–2.581(2) Å and, once again, the distances to the more substituted carbons (C2 and C12) are longer than those to the exocyclic methylene carbons (C10 and C20). The silver atoms complex to the less hindered face of the double bond, in both the coordinated molecules of **2**. These two structures serve to show that chiral, discrete silver complexes can readily be prepared in which the silver atom coordinates to either an endocyclic double bond (as in **5**) or an exocyclic double bond (as in **6**).

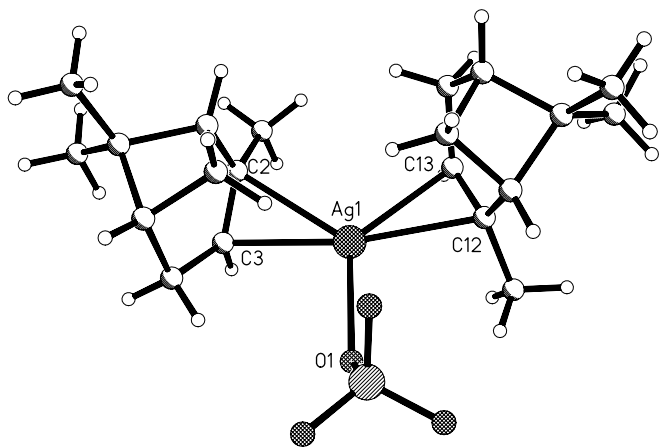


Fig. 1. Perspective view of the X-ray crystal structure of **5** formed from (1S)-(-)- $\alpha$ -pinene. Selected interatomic distances (Å): Ag1–C2 2.515(4), Ag1–C3 2.402(5), Ag1–C12 2.500(4), Ag1–C13 2.402(4), Ag1–O1 2.397(3).

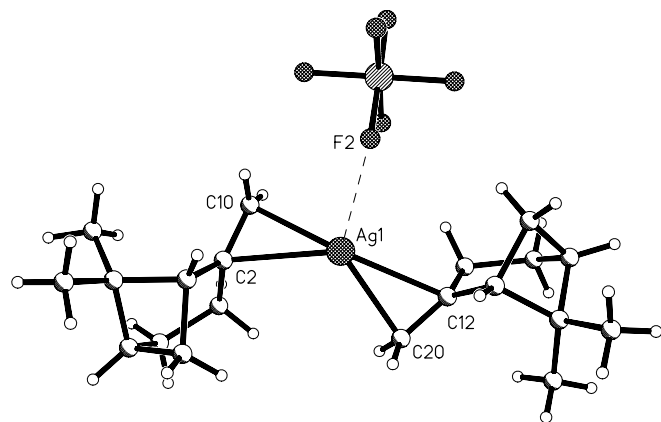


Fig. 2. Perspective view of the X-ray crystal structure of **6** formed from (1S)-(-)- $\beta$ -pinene. Selected interatomic distances (Å): Ag1–C2 2.581(2), Ag1–C10 2.303(3), Ag1–C12 2.513(2), Ag1–C20 2.296(3), Ag1–F2 2.686(2).

In order to extend this synthetic approach from discrete mononuclear complexes to multinuclear coordination polymers of higher dimensionality, the organic ligand needs to act in a bridging mode. As we have shown recently, this requires the use of dienes as bridging ligands between silver centres [4]. Thus, the two readily available monoterpene dienes  $\gamma$ -terpinene (**3**), and (R)-(+)-limonene (**4**), were investigated as potential bridging ligands for silver-based coordination polymers. The achiral diene **3** was reacted with several silver salts and the product from reaction with silver hexafluorophosphate was found to form a discrete mononuclear complex (**7**). This compound crystallizes in the centrosymmetric monoclinic space group  $C2/c$ , with the asymmetric unit containing a molecule of  $\gamma$ -terpinene, half a silver atom and half a hexafluorophosphate counterion both of which lie on a twofold rotation axis. Thus, the actual structure is a discrete  $L_2M$  complex similar to **6** (Fig. 3) and also has approximately linear coordination of the two double bonds to the silver which interacts only weakly with the counterion. The most surprising feature of this structure is that the silver coordinates to the more hindered of the two double bonds within the monoterpene. This is presumably because it is the more electron rich due to the greater electron donating ability of the isopropyl substituent compared to the methyl group. This electronic effect apparently overrides the steric effects. As with the other structures, the bond from the silver atom to the less substituted carbon of the double bond is shorter than the other.

Reaction of  $\gamma$ -terpinene with silver(I) triflate furnished a product **8** as thin, unstable plates, most of which were highly twinned. After many attempts a data set was extracted from one of several collections which was sufficient to reveal the structure to be a two-dimensional coordination polymer, albeit achiral. Fig. 4 shows the contents of the asymmetric unit, which contains one molecule of  $\gamma$ -terpinene and two silver atoms bridged by two bidentate triflate anions with a silver–silver separation that is

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